

Enhancement of visible light photocatalytic activity of MoO₃ with V₂O₅ additive

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Abstract— Both MoO₃ and V₂O₅ exhibit considerable absorption in the visible region as seen from their UV-visible diffuse reflectance spectra. In view of higher absorption of V₂O₅ compared to MoO₃, the present study is taken up to see whether addition of V₂O₅ will improve the visible light photocatalytic activity of MoO₃. 25 wt% V₂O₅ in MoO₃ showed the highest efficiency and degraded Methyl orange, Rhodamine-B and Eosin Y completely in 30, 160 and 40 mins respectively, while Methylene blue is only partially degraded..

Index Terms— MoO₃, V₂O₅, Rhodamine-B, Methylene blue, Methyl orange, Eosin-Y, Photocatalysis

I. INTRODUCTION

Semiconductor mediated photocatalytic oxidation of organic pollutants has attracted worldwide scientific research because of the ease of performance of reaction at ambient conditions exploiting the inexhaustible solar radiation that provides a cost effective clean technology. Among the binary metal oxide semiconductors, TiO₂ is proved to be the most suitable photocatalyst for non-selective mineralization of several mutagenic/carcinogenic hazardous organic pollutants present in industrial waste water effluents. TiO₂ is useful because it is inexpensive, photo stable, non-toxic, chemically inert and easy to synthesize.

However, major drawback of TiO₂ is its relatively small absorption in the visible region due to its wide band gap of 3.2eV requiring U.V radiation of < 380nm for excitation. Since U.V. radiation is < 5% of solar radiation, intensive research efforts were focused to render TiO₂ into a visible light active photocatalyst either through suitable doping, or addition of a sensitizer or by forming a nano/meso composite [1]. Alternately, photocatalysts from other binary metal oxides ZrO₂ [2], MnO₂ [3], NiO [4], Fe₂O₃ [5], ZnO [6], CO₃O₄ [7], WO₃ [8], SnO₂ [9], CdO [10], Bi₂O₃ [11], CeO₂ [12], La₂O₃ [13] as well as mixed metal ternary oxides such as ZnWO₄ [14], BiVO₄ [15], Bi₂MoO₆ [16], Bi₂WO₆ [17], Bi₂Mo₃O₁₂ [18], Fe₂Mo₃O₁₂ [19] etc with band gap suitable for absorption in the visible region of solar radiation are also being explored. Recently, the authors reported a comparative study of visible light photocatalytic activities of MoO₃, Cu₂O and V₂O₅ against Degusa P25 [20]. The study revealed that photocatalytic activities of the above catalysts varied in the order TiO₂<MoO₃<Cu₂O<V₂O₅ for the degradation of

Rhodamine-B, Methylene blue, Methyl orange and Eosin Y. The present study is taken up to explore whether addition of V₂O₅ because of its lesser band gap compared to MoO₃ will enhance the efficiency of MoO₃ towards photocatalytic degradation of Rhodamine-B (Rh-B), Methylene blue (MB), Methyl orange (MO) and Eosin-Y (EY).

II. MATERIALS AND METHODS

Samples of A.R grade MoO₃, V₂O₅, Cu₂O and TiO₂ (Degusa P-25) as purchased are used in the photocatalytic studies.

A. Characterisation Techniques

Phase purity of MoO₃ was investigated with X-ray diffractometer (PANalytical- X' Pert PRO, Japan) at room temperature, using Nickel filtered Cu-K_α radiation ($\lambda = 1.54059 \text{ \AA}$), with a scan rate of 2° min^{-1} . UV-visible diffuse reflectance spectrum (UVDRS) of the sample was obtained with dry pressed disk samples using Shimadzu UV-visible spectrophotometer (UV-3600) between 200 to 800 nm range. Spectral grade BaSO₄ was taken as reference in the UV-DRS.

B. Photocatalytic Studies

100 mg of catalyst powder was added into 100 ml Rh-B aqueous solution (5 mg/L). The suspension was magnetically stirred for 30 minutes in dark. The suspension was then exposed to 400 watts metal halide lamp; 5ml aliquots were pipetted at periodic time intervals and filtered through 0.45 micron Millipore filters to remove the suspended powder. Progress of decoloration was followed by recording the corresponding absorption spectra. The same procedure has been adopted for (10mg/L) MB, MO, Rh-B and EY dyes. All the experiments were conducted under ambient conditions. Extent of degradation of dye is calculated by using the expression.

$$\% \text{ degradation} = (A_0 - A_t) / A_0 \times 100$$

where A₀ and A_t are respectively initial absorbance and absorbance at time 't'

III. RESULTS AND DISCUSSION

MoO₃ is known to exist in three polymorphic forms-namely α (orthorhombic), β (monoclinic) and h (hexagonal). The sample used in the present study is orthorhombic as identified from its XRD pattern shown in Fig. 1.

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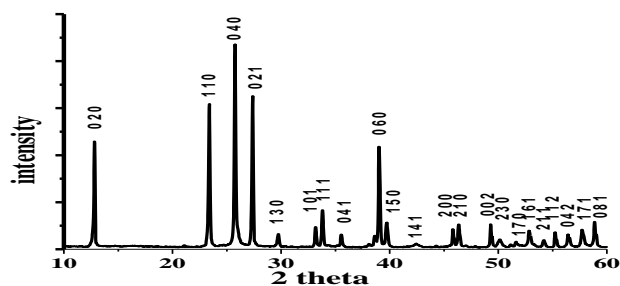


Fig 1. XRD pattern of MoO₃ sample used.

Temporal variations of spectral contours for methyl orange aqueous solution + MoO₃ as a function of irradiation time in presence and in absence of H₂O₂ are depicted in Fig 2.

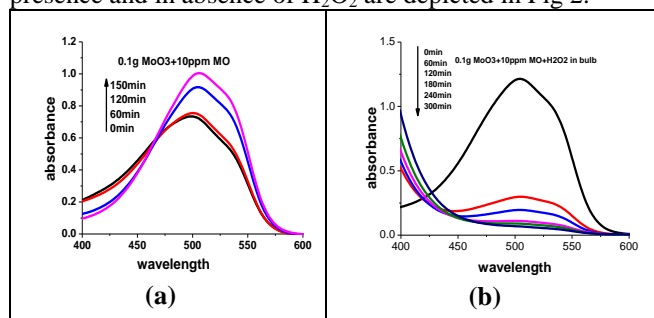


Fig. 2. Temporal variation of spectral contours of aqueous solution of MO+MoO₃ as a function of irradiation time (a) in the absence and (b) in the presence of H₂O₂

From the figure it can be seen that in the absence of H₂O₂, the decrease in absorption intensity is very less indicating no significant dye degradation for exposure up to 150 minutes. However, in presence of H₂O₂, there is 98 % decrease in intensity for 180 min of exposure. In photocatalytic process, presence of external oxidant H₂O₂ has been found to be beneficial in several photocatalytic studies over TiO₂ [21], Bi₂Mo₃O₁₂ [22] and Fe₂Mo₃O₁₂ [19]. H₂O₂ increases the electron-hole recombination time by accepting the conduction band electrons in the catalyst to form $\cdot\text{OH}$ radicals which act as powerful oxidants and attack dye molecular frame work and disintegrate it. This provides an additional way for degradation process besides the dye degradation due to e^- directly. The enhanced activity due to H₂O₂ is attributed to the following reactions.

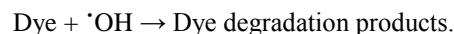
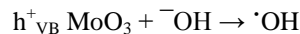
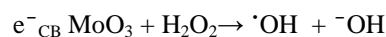


Fig. 3 shows temporal variation of spectral contours for MO aqueous solution with 5, 10, 20 and 25 wt% V₂O₅ in MoO₃. From the figure, it can be seen that complete decoloration in these cases occurred for 180, 100, 90 and 30 min respectively.

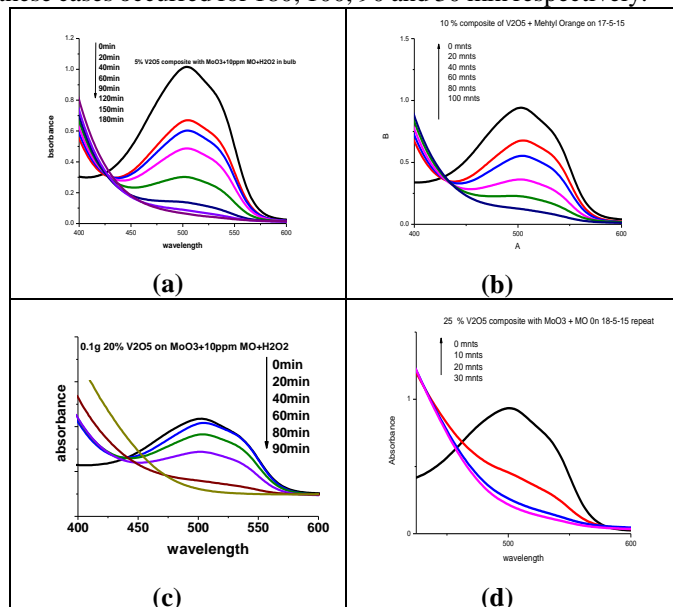


Fig. 3. Temporal variation of spectral contours for MO aqueous solution with (a) 5wt% (b) 10wt% (c) 20wt% and (d) 25wt% V₂O₅ as a function of irradiation time

The observed decrease in lowering of degradation time could be understood in terms of the UV-visible diffuse reflectance spectra of V₂O₅, MoO₃ and 25 wt% V₂O₅ in MoO₃ shown in Fig. 4. Since V₂O₅ shows higher absorption compared to MoO₃ in the visible region up to ~550 nm, the observed increase in catalytic efficiency for 25 wt% V₂O₅ in MoO₃ is attributed to the additive.

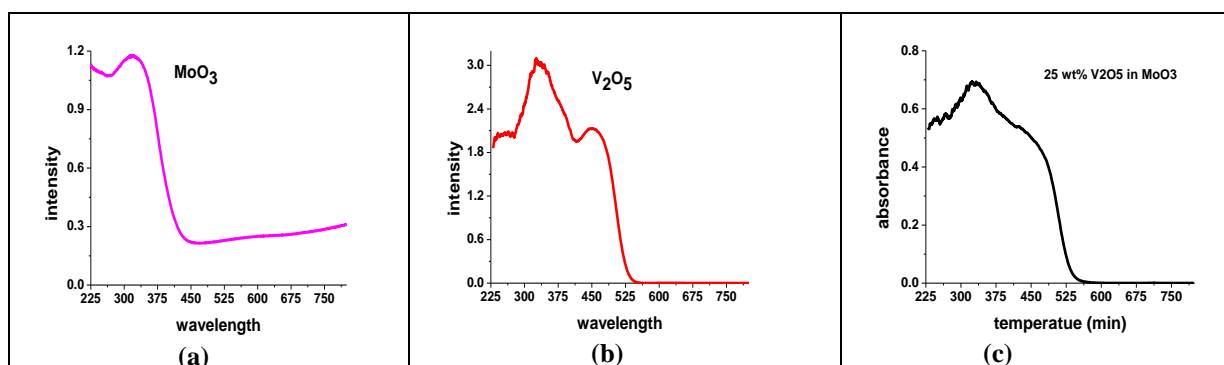


Figure 4. UV-visible diffuse reflectance spectra of (a) MoO₃, (b) V₂O₅ and (c) 25 wt% V₂O₅ in MoO₃

Fig 5 shows UV-visible absorption spectra at different times for Rh-B, MB nd EY with H₂O₂ over MoO₃ containing 25wt% V₂O₅ under progressive irradiation.

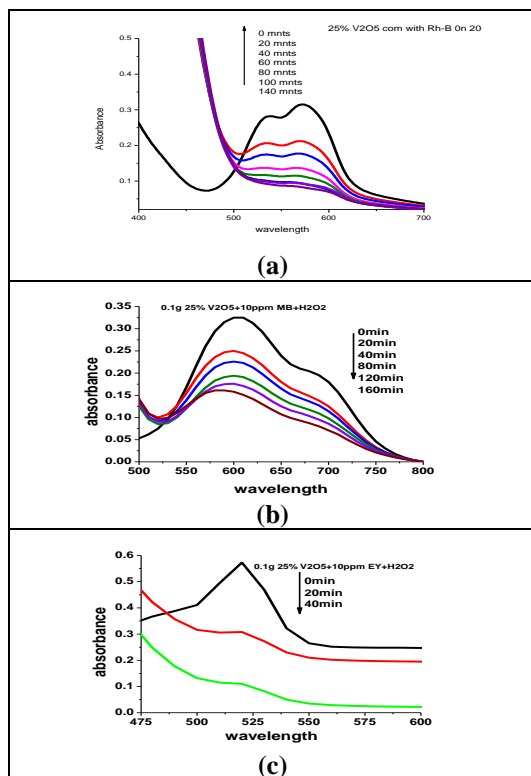


Fig. 5. Variation of spectral intensities as a function of irradiation time for (a) Rh-B, (b) MB and (c) EY.

From the figure it is apparent that 25 wt% V_2O_5 in MoO_3 is very effective in decolorizing Rh-B and EY for 140 and 40 min of irradiation while MB is degraded only to an extent of 51.3% for 160 min of irradiation. The obtained experimental data suggests that the photocatalytic efficiency of MoO_3 can be enhanced by mixing of V_2O_5 to an extent of 25 wt%.

IV. CONCLUSIONS

Samples of 5, 10, 20 and 25 wt% of V_2O_5 in MoO_3 were evaluated for photocatalytic degradation of Methyl orange in presence of H_2O_2 . The degradation times for complete decolorisation gradually decreased from 180 to 30 min with 5 wt% to 25 wt% respectively. 25 wt% V_2O_5 in MoO_3 has been successful in effecting ~ 100% photocatalytic degradation of Methyl orange, Rhodamine-B, Eosin-Y and partial degradation in Methylene blue.

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